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遅い緩和過程：モード結合と動的密度汎関数法*

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はじめに

だいたい前に物性研究編集部から表題に関連したテーマについて執筆する様依頼があった。一応承諾したものの、執筆する余裕がないまま日がたってしまった。そこで編集部と相談して、今回はこれまで色々な折りに書きためてあった英文の文書を集めて編集したもので代用させて戴くことにした。要旨は以下の通りである。

先ず全く関係がない様に見える気体の輸送現象から話をはじめ。周知の様に希薄気体の輸送理論は百年前のボルツマン方程式から始まる。第二次大戦後になってこれをリウビユ方程式から基礎づけ、同時に高密度へ拡張する試みが始まった。後者は不完全気体のビリアル展開の非平衡への拡張である。所が予想に反してビリアル展開は不可能である事がわかった。という事は気体に於いても多数の粒子の協力的運動が無視できない事を意味する。一方気体と対極にあるのが臨界点近傍の系である。ここでは粒子の相関が数千オングストロームにも及び、はじめから多粒子の集団運動を考えねばならない。これを非平衡の問題に取り入れる手段としてモード結合理論(MCT)が考えだされた。臨界現象がくりこみ群の出現により解決されればMCTもその役割を終える。所が実はこの理論がそれまで難問とされていた古典液体のダイナミクスに使える事がわかり、更にその延長として過冷却液体やガラス転移もその守備範囲に入る事が指摘されMCTが再び脚光を浴びる事になった。ただし今度は臨界現象と違って危険な領域に足を踏み込む事になる。即ち問題にする長さのスケールが微視的な長さに近く、本来MCTの様な連続体的な記述はなじまない。したがって考え方の上では微視的なスケールの問題を連続体として扱う密度汎関数理論に近い。ここに動的密度汎関数理論(DDFT)が登場する事情がある。ただし現存のDDFTはまだ原始的で問題点が多い。そもそも連続体としての取扱い是一种の粗視化である。その時の最重要な問題は粗視変数をどう選ぶかである。これについてきちんとした議論はまだ無い様である。とりあえず粒子数密度、運動量密度、エネルギー密度を粗視変数の候補と考えると高密度液体では粒子数密度のみが遅い変数になるという議論があり、エンスコグ理論による計算もある。しかし他に重要な変数、例えばストレステンソルの様なもの、を考えなくてよいのか自明ではない。今後のより立ちいった研究がのぞまれる。最後から3番目と2番目の章では液体及びスピン系でDDFTを微視的に導く試みを述べたが今の段階ではフォーマルである。

* 本稿は、編集部の方から特にお願いして執筆していただいた記事である。

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1 Prologue

In 1964 I joined Irwin Oppenheim's group at MIT as a postdoc. At that time there was a great interest in U.S. and also in parts of Europe in kinetic theory of non-dilute gas, while in Japan there was practically no interest on this topic. So I had to learn from the very beginning starting with reviewing the Boltzmann equation. My problem given by Irwin was to calculate the first density correction to shear viscosity of gas starting from the Green-Kubo formula and to see if the result differs from the Choh-Uhlenbeck result. There were still discordant noises against Green-Kubo formulae, and it was of fundamental importance to examine validity of such formulae. We hoped to make a new discovery by finding some difference. In contrast to the task of finding density corrections to equation of state which is rather easy, the situation is totally different here. After all three body dynamics is an unsolved problem in classical mechanics. After excruciating efforts we obtained the final result which was in complete agreement with the classic work of Choh-Uhlenbeck. After this work was finished, we had a visitor from National Bureau of Standards (now NIST), Jan Sengers who is now at University of Maryland, and told us a startling story. He said that the first density corrections to transport coefficients of two-dimensional gas diverge! This implies that the basis for the virial expansion in which each coefficient in this expansion involves only a finite number of molecules is untenable for transport coefficients, and hence one has to take into account processes involving indefinite numbers of molecules from the outset (resummation over the so-called ring collisions). Without realizing at that time, we were at the end of what I called elsewhere the ancient period of non-equilibrium statistical mechanics [1] where we believed that there is a clear-cut separation of microscopic and macroscopic length and time scales which underlies all the macroscopic dynamical laws. As a matter of fact, subsequent developments revealed very rich structures in the region which is neither microscopic nor macroscopic but may

be called mesoscopic¹. The archetypical example where this kind of collective processes plays a major role is critical dynamics. In critical phenomena, even equilibrium properties are already dominated by long wavelength fluctuations involving a great many numbers of particles. Thus here the method that permits treatment of such "mass" is needed. In order to explain an essence of the method, we start from a general Green-Kubo type formula for an Onsager kinetic coefficient L as follows:

$$L = V^{-1} \int_0^\infty dt \langle J(t)J(0) \rangle \quad (1.1)$$

where V is the system volume, $J(t)$ is a microscopic expression for an appropriate flux, and the angular bracket stands for equilibrium average. Now, by construction, J is orthogonal to all the macroscopic variables (their corresponding microscopic expressions) A which are often referred to as "gross variables"²:

$$\langle JA \rangle = 0 \quad (1.2)$$

Otherwise, the integrand of (1.1) would not decay to zero in a short time and the time integral diverges. The condition (1.2) alone, however, does not guarantee that the integrand of (1.1) always decays to zero rapidly because it only demands that J be orthogonal to the first power of A and not to the higher powers. In fact important contributions do arise from the components of J which contain such higher powers of A because when A is slowly-varying, then its products are expected to contain slowly-varying components. An outstanding example of this is the divergence of thermal conductivity of fluid at its critical point, where the density fluctuation develops a diverging correlation length which we denote as ξ . A Green-Kubo expression for the

¹The term mesoscopic is now quite often used to designate a group of quantum-mechanical phenomena which are not microscopic. Here we use the term differently but is perhaps more appropriate.

²Equilibrium averages of A are always assumed to be subtracted off. That is, A only contains fluctuation from equilibrium

thermal conductivity is

$$\lambda = \frac{1}{k_B T^2} \int d\mathbf{r} \int_0^\infty dt \langle j_x(\mathbf{r}, t) j_x(0, 0) \rangle \quad (1.3)$$

where $j_x(\mathbf{r}, t)$ is the x -component of heat current density. Then its slowly-varying component is simply given by $T\delta s(\mathbf{r}, t)v_x(\mathbf{r}, t)$, where $\delta s(\mathbf{r}, t)$ is the local specific entropy fluctuation and $v_x(\mathbf{r}, t)$ the x -component of the local velocity fluctuation. Here it is more convenient for dynamics to use the specific entropy fluctuation as the order parameter fluctuation rather than the more usual density fluctuation. Substituting this result into (1.3) and assuming mutual statistical independence of entropy and velocity fluctuations, the rhs of (1.3) is simply calculated and is expressed in terms of the specific heat at constant pressure. In this way one finds that λ behaves near criticality roughly as ξ . The theory outlined here is now known as the mode coupling theory (MCT). Following the initial suggestive calculations of M. Fixman [2] in the early sixties, the modern MCT as we see it today was developed by various authors from mid sixties to early seventies, and was reviewed, for instance, by the author [3] and by Keyes [5]. The name comes from the decomposition of flux J , which is essentially time derivative of a gross variable, into products of gross variables. A gross variable physically represents a type of disturbance in an equilibrium system, which can be called a "mode". This naming was initially suggested from plasma turbulence theory. The intuitive way of constructing the mode coupling expression of the heat flux density given above can be formalized by making use of the fact that J is related to time derivative of a gross variable \dot{A}_i where an overdot is differentiation with respect to time and different gross variables are distinguished by suffices. The mode coupling contribution $(\dot{A}_i)_{MCT}$ of \dot{A}_i is then written in the two-mode approximation as

$$\begin{aligned} (\dot{A}_i)_{MCT} &= \frac{\langle \dot{A}_i A_j^* A_k^* \rangle}{\chi_j \chi_k} A_j A_k \\ &= \frac{k_B T \langle \{A_i, A_j^* A_k^*\}_{PB} \rangle}{\chi_j \chi_k} A_j A_k \end{aligned} \quad (1.4)$$

where $\chi_i \equiv \langle A_i^* A_i \rangle$ with $\langle A_i^* A_j \rangle = 0$ for $i \neq j$, and $\{\}_{PB}$ is a Poisson bracket and an asterisk $*$ is complex conjugate. Since the rhs of (1.4) involves only static quantities, this is called *reversible* mode coupling, whereas there are other types of nonlinearity called *dissipative*

mode coupling and will be discussed later. These two types of mode coupling will produce rather different consequences as we shall see.

Now, there is a more general and exact expression for reversible mode coupling. This is obtained by considering the instantaneous rate of change of A_i averaged over the constrained equilibrium state such that $A_j = a_j$ for all j . This is denoted as $\langle \dot{A}_i; \{a\} \rangle$ where $\{a\}$ denotes the set of fixed values of all the A 's. Then it can be shown that

$$\begin{aligned} \langle \dot{A}_i; \{a\} \rangle &= - \sum_j \left(k_B T \frac{\partial}{\partial a_j} \right. \\ \langle \{A_i, A_j\}_{PB}; \{a\} \rangle &- \left. \langle \{A_i, A_j\}_{PB}; \{a\} \rangle \right. \\ &\times \left. \frac{\partial H\{a\}}{\partial a_j} \right) \end{aligned} \quad (1.5)$$

where $H\{a\}$ is the free energy functional associated with the local equilibrium distribution function $D_l\{a\}$ through $(\beta \equiv 1/k_B T)$

$$H\{a\} \equiv -\beta \ln D_l\{a\} \quad (1.6)$$

$$D_l\{a\} \equiv \langle \prod_i \delta(A_i - a_i) \rangle \quad (1.7)$$

The previous result (1.4) follows if we expand the above equation in a at the second order. The general expression (1.5) first appeared in author's article of Varenna School [6] and has since appeared repeatedly in literature. The full nonlinear stochastic equation of motion for A in the two-mode approximation takes the form,

$$\begin{aligned} \dot{A}_i &= - \sum_j L_{ij}^0 \frac{\partial H\{A\}}{\partial A_j} \\ &+ \frac{k_B T \langle \{A_i, A_j^* A_k^*\}_{PB} \rangle}{\chi_j \chi_k} A_j A_k + \zeta_i \end{aligned} \quad (1.8)$$

where L_{ij}^0 is the bare Onsager kinetic coefficient and ζ_i is the thermal noise related each other by the following fluctuation-dissipation theorem:

$$\langle \zeta_i(t) \zeta_i^*(t') \rangle = 2L_{ij}^0 \delta(t - t') \quad (1.9)$$

This stochastic equation, together with the factorization approximation which decomposes a correlation of the four A 's into a sum of products of two pair correlations of the A 's gives rise to a self-consistent equation for $\langle A_i(t) A_j^*(t') \rangle$. This is the self-consistent mode coupling equation, and has been used in critical dynamics

since the late sixties. The choice of gross variables is dictated by their slow time variations. Thus in critical dynamics we can choose conserved variables and non-conserved order parameter variables if any. This mode coupling idea of critical dynamics mentioned above was combined with renormalization group theory of equilibrium critical phenomena initiated by K. Wilson into the dynamical renormalization group theory [4]. This development marked an end to critical dynamics as a frontier of physics around 1980.

Concurrently with the developments of critical dynamics, people noted some peculiarities of transport phenomena even away from criticality. For instance, in two-dimensional fluids transport coefficients generally diverge, and even in three-dimension, coefficients of next gradient expansions in macroscopic laws (so called Burnett coefficients) again show divergences. This is the famous long-time-tail problem and was reviewed by Pomeau and Résibois [7]. This long time tail phenomena can be naturally understood in the framework of mode coupling where only conserved variables come into play. However, there was an unexpected surprise. If the long time contributions of time correlation functions entering Green-Kubo formulae are examined by molecular computer simulation, the coefficients of such contributions which behave in time like $t^{-1/d}$, d being dimensionality of space, turned out to be always greater by two orders of magnitudes [8]. Resolution to this dilemma came a few years later from the two independent works by T. Kirkpatrick [10] and by H. van Beijeren [11]. They have shown that what was seen in molecular dynamics is not the genuine long time tail predicted by the conventional MCT but the intermediate time structural relaxation of liquids which can be understood by extending MCT to deal with such phenomena where two-density modes play crucial whereas in the usual long time tail the velocity field is involved as one of the coupled modes.

Independently of these developments, kinetic theory of dense gas and liquids were being developed by several people where mode coupling mechanism naturally occurs in which the same two-density-mode plays an important role. Combined with separate microscopic treatments of short time behavior, this kinetic theory is reasonably successful in quantitatively accounting liquid dynamics like various transport coefficients and time correlation functions that can be measured by scattering experiments [9].

2 Mode Coupling Theory of Supercooled Liquids and Glass Transitions

With the developments described in the preceding section as precursors, it is natural that these theoretical methods are applied to supercooled liquids and glass transitions. This took place in 1984 [12, 13]. This is now known as the mode coupling theory of glass transitions and is unique among theories of structural glass transitions in the sense that the theory gives specific predictions starting from first principles which can be tested experimentally as well as by computer simulations. Some recent advances are reviewed by Götze and Sjögren [14] and most recently by Kob [15].

The theory deals with the autocorrelation function of the density fluctuation $\hat{\rho}_{\mathbf{k}}$ where $\mathbf{k} \neq 0$ is the wave vector of the Fourier transform of the local density and $\hat{\cdot}$ means a microscopic expression, that is, for an assembly of N particles located at $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N$

$$\hat{\rho}_{\mathbf{k}} = \sum_{j=1}^N e^{i\mathbf{k} \cdot \mathbf{r}_j} \quad (2.1)$$

The normalized density autocorrelation function $\phi_{\mathbf{k}}(t)$ is defined by

$$\phi_{\mathbf{k}}(t) \equiv \langle \hat{\rho}_{\mathbf{k}}(t) \hat{\rho}_{-\mathbf{k}}(0) \rangle / S_{\mathbf{k}} \quad (2.2)$$

$$S_{\mathbf{k}} \equiv \langle \hat{\rho}_{\mathbf{k}}(0) \hat{\rho}_{-\mathbf{k}}(0) \rangle \quad (2.3)$$

where $S_{\mathbf{k}}$ is the static scattering structure function. The density autocorrelation function is the quantity of central interest here since this gives information about freezing and is directly accessible by scattering experiments. MCT aims at obtaining this quantity theoretically by deriving a self-consistent equation for it. We here derive it following the method originally used by Götze and the coworkers [14] and starts from the following Zwanzig-Mori type exact identity for $\phi_{\mathbf{k}}(t)$:

$$\frac{d^2}{dt^2} \phi_{\mathbf{k}}(t) = -\omega_{\mathbf{k}}^2 \phi_{\mathbf{k}}(t) - \int_0^t dt' M_{\mathbf{k}}(t-t') \frac{d}{dt'} \phi_{\mathbf{k}}(t') \quad (2.4)$$

where

$$\omega_{\mathbf{k}} \equiv k[k_B T \rho_0 / m S_{\mathbf{k}}]^{1/2} \quad (2.5)$$

is the frequency of short time molecular oscillation, ρ_0 and m being the average number density and molecular mass, respectively, and $M_{\mathbf{k}}(t)$ is

the memory function expressed as a time correlation function of random force governed by projected dynamics. The MCT approximation consists of expressing the random force as a nonlinear function of the density fluctuation in the form of (1.4) and then making factorization approximation of the type used by the author [16], which results in the memory function of the form $M_k(t) = \mathcal{F}_k\{\phi(t)\}$, $\mathcal{F}_k\{f\}$ being a functional of f . This together with (2.4) constitutes the self-consistent MCT equation. This is a so-to-speak single step method from microscopic description to MCT equation. Thus it is not easy to improve on approximations such as factorization approximation.

A different derivation is based on the dynamical extension of the density functional method of inhomogeneous fluid, which is motivated by the fact that in deeply supercooled liquid the density is the slowest variable. The simplest version of the so-called dynamical density functional theory (DDFT) is the following equation for the density probability functional $P(\{\rho\}, t)$

$$\frac{\partial}{\partial t} P(\{\rho\}, t) = -L \int d\mathbf{r} \frac{\delta}{\delta \rho(\mathbf{r})} \nabla \cdot \rho(\mathbf{r}) \nabla \left[T \frac{\delta}{\delta \rho(\mathbf{r})} + \frac{\delta H\{\rho\}}{\delta \rho(\mathbf{r})} \right] P(\{\rho\}, t) \quad (2.6)$$

where L is the kinetic coefficient that incorporates rapid temporal variation of the momentum density field. See also a review [25]. This is again a highly nonlinear stochastic field equation, but one can still derive from it the self-consistent MCT equation. The simplest way of doing this seems to be to use the irreducible memory function method [21]. Since the nonlinearity entering here is purely dissipative, derivation by applying mode coupling approximation (MCA) to the conventional memory function to obtain a self-consistent equation such as that found in Munakata's paper [25] is quite misleading. The warning against such uncritical use of MCA to deal with dissipative nonlinearities was illustrated by various examples by Jäckle and his coworkers [33]. The current status of MCT of supercooled liquids and glass transitions in relation to experimental and computational findings is taken up in numerous recent review articles [14, 15, 34, 41], and thus will not be discussed here. The overall impression is that although MCT is definitely successful in capturing initial stages of freezing toward glass transitions, it is not easily extendable to the regime where the viscosity reaches to 10^{13} poises and to non-

fragile glasses despite some successes with MCT analyses of experiments.

3 Beyond MCT: Mesoscopic Kinetic Equation

In view of what was said about MCT in the preceding section, it is apparent that we must reexamine the basis of the current MCT approach, which in my opinion is still in a rather primitive stage of developments despite an explosion of literature on the subject. Thinking about what should be done to the theory next, it is useful to recall the situation in critical dynamics as was described in the preceding section. The current state of MCT in glass can be compared to the self-consistent MCT of critical dynamics of the late sixties[19]. Although the problem of supercooled liquids and glass transition is sufficiently different from critical dynamics, it seems that the next natural step beyond the current MCT should be construction of appropriate MKE for supercooled liquids and possibly glass. The major problem confronting us in this endeavor is the choice of proper gross variables. In critical dynamics, this is not a serious problem because we know with confidence that the densities of all the conserved quantities and the variables associated with spontaneous breakdown of continuous symmetries of phase transitions (the Goldstone modes) if any constitute good candidates of the gross variables. In supercooled liquids and glass transitions, this is far less trivial precisely because one has to deal with the short length scale behavior of the order of intermolecular distances. Regarding this problem, Cohen and de Schepper [22] gave a heuristic argument for the choice of gross variables for dense hard sphere fluids. They argued that in sufficiently dense fluids where molecules are jammed together and are difficult to move around, the local momentum and energy densities (more precisely, the part of the energy density which is not coupled to the mass density) can still be quickly transferred among the molecules. However, the (number or mass) density change on the scale of the intermolecular distance must accompany a major local rearrangement of molecules requiring passing over of a high potential barrier, hence is not easy, and thus the (number or mass) density, which will be referred to simply as the density in the following, should be a slowly-varying variable. This

heuristic argument is substantiated by the calculations of normal modes of linearized revised Enskog theory of dense hard sphere fluid[23, 24]. The usual three hydrodynamic modes coupled to the density, that is, one heat mode and two sound wave modes, are the slow modes at small wave numbers well separated from other non-conserved modes. As the wave number increases toward 2π divided by the hard sphere diameter, only the heat mode remains as a slow mode, other modes being buried in fast-decaying non-conserved modes. This heat mode is precisely the non-propagating part of the density mode. One additional support for this argument can be found in the generalized kinetic theory of dense fluid[9]. One looks at the memory functions entering the equations for time correlation functions of momentum variables. The vertices that connect momenta to other slow variables automatically pick up only the density variable. Thus the latter variable is slowed down in a self-consistent manner. See the argument on p. 168 of [9].

If one accepts these arguments that the density is the only relevant slow variable, then there must be a kinetic theory in which the density is the only gross variable. Here I draw attention to the density functional theory (DFT) which was developed originally for inhomogeneous fluids[45]. DFT can be regarded as a kind of the familiar Landau theory of phase transitions[30] where one assumes a smooth free energy function which contains in addition to the conventional thermodynamic variables an extra variable which is an order parameter of phase transition. Singular behavior associated with a phase transition

results when one minimizes the free energy function with respect to the order parameter. Thus, mathematically, a phase transition is understood as a bifurcation of the solution of the equation which expresses the minimization condition of the free energy function. In our case the order parameter is the local density and the free energy function is replaced by the free energy *functional* since we must allow spatially inhomogeneous density distributions. We then minimize the free energy functional with respect to the density function under appropriate conditions such as the fixed total mass of the fluid. This gives rise to a nonlinear functional equation for the density profile which contains the intensive thermodynamic variables like temperature and pressure as control parameters. If

the solution is the uniform density for a given set of control parameters, we have a liquid state. If we obtain a spatially periodic solution, we have a crystalline solid. In some cases we find irregular inhomogeneous density profiles[31, 32]. Then we have an amorphous solid. In this way DFT successfully predicts equilibrium phase behavior and other equilibrium properties. It should be noted that DFT is precisely the theory that deals with small scale structures within the continuum framework. Thus it is a natural framework to study glasses as well where short and intermediate scale structures are relevant.

However, DFT has no dynamics, and hence its dynamical extension is necessary to deal with glass transition, which is a highly dynamical phenomenon as many experiments have shown. We have thus proposed such a kinetic equation which we call the dynamical density functional (DDF) equation (2.6)[20]. Essentially the same equation was proposed before in other contexts in[26, 27]. However, its relevance for MCT of Götze and others were realized only recently in [20]. We also note that the stochastic equation having a quite similar spirit where fast variables are eliminated first in favor of slow variables was proposed much earlier[28]. In all these cases one always has to ascertain that the variables eliminated are indeed fast. Otherwise one should start from formally exact equation with memory to be discussed below.

The formally exact version of this DDFT equation (2.6) can be directly derived starting from a microscopic Liouville equation for an assembly of N particles. Since this derivation is rather lengthy and will be published elsewhere[29], this will not be repeated but will be sketched with a few additional materials in Section 5. (A microscopic derivation of DDFT equation starting from the Smoluchowski equation with and without hydrodynamic interaction are also given in [29].) This is most satisfactory if we can justify that the density is the only slow variable for a high density fluid at short distance [22].

4 Lattice Gas Version of DDFT

The DDFT equation is the most natural equation that embodies the idea that in sufficiently dense fluids the density is the only slow variable that describes local small scale motions.

From this point of view, the recent computational works[35, 36] that simulate the Langevin equation containing the momentum and density variables at relatively short times and then switch to the Monte Carlo simulation which uses the Ramakrishnan-Yussouf type density functional as the energy at longer times are not quite satisfactory for studying glassy slow dynamics in supercooled dense liquids.

In our DDFT approach[20, 21] we at the outset analytically eliminate the momentum variable which varies rapidly and obtain a closed stochastic equation containing only the density variable. This single dynamical equation includes the nonlinear feedback mechanism of the mode coupling theory (MCT), and at the same time permits to study long time behavior even in glassy regions which are governed by thermally activated processes over free energy landscape generated by $H\{\rho\}$. We have argued in [37]³ and will be shown that our DDFT equation can be mapped onto a spin exchange type kinetic Ising model which can be studied by the standard Monte Carlo simulation method, where spin exchanges take place with equal probability between any pair of spins belonging to the nearest neighbor coarse graining cells. (Mapping of general kinetic Ising model onto a DDFT type continuum stochastic model is described in Section). The energy entering the Ising model denoted as $E_0(\mathbf{n})$ is, with \mathbf{n} the total set of lattice gas occupation numbers $n_i = 0, 1$ with i the lattice points $1, 2, \dots, M$,

$$E_0(\mathbf{n}) = -\frac{1}{2}\beta^{-1} \sum_{i \neq j} C_{ij} n_i n_j, \quad (4.1)$$

where $C_{ij} \equiv c(\mathbf{r}_i - \mathbf{r}_j)$ is the direct correlation function in the liquid theory which appeared in (3.3). Here we note the following inequalities among the lattice constant h , the coarse-graining length a and the range of C_{ij} denoted as σ and the inter-particle distance $l \sim \rho^{-1/3}$, ρ being the number density:

$$h \ll a \ll \sigma \sim l \quad (4.2)$$

If we map the lattice gas onto spin-exchange kinetic Ising model, the nonlinear feedback mechanism of MCT enters here through the use of

³We would like to make two corrections in this reference: (1) the \ln sign in Eq.(4.2) should be moved to the inside of $[\]$ to the right. (2) The word "atoms" in the 4th line from the bottom of page 7 must be replaced by the word "lattice points".

spin-exchange dynamics but not the Glauber type dynamics of single spin flips, which is responsible for the factor $\rho(\rho_m - \rho) \cong \rho_m \rho$ in the Fokker-Planck equation of DDFT,(3.2). The consideration above gives an intriguing possibility. The usual density functional such as that of Ramakrishnan and Yussouf is obtained by coarse-graining our Ising Hamiltonian. Thus if DFT is going to exhibit interesting phase behavior like freezing or glassy behavior, this must be reflected in some way in our Ising Hamiltonian. Thus the studies of our Ising-like models as a substitute of DFT might be quite rewarding.

In our lattice gas model, the nonlinear feedback mechanism of density arrest central to MCT is seen to be a consequence of the exclusion or steric hindrance property of spin exchange or particle migration in the lattice gas language⁴. This property is in fact quite universal to molecular systems having strong short range repulsive interaction. This correspondence appears to be related to the observed universality. From this point of view, one may conjecture that the major role of complexities of glass-forming molecules or presence of polydispersivity in colloidal glasses is to prevent crystallization. However, the details such as the values of exponents or so-called hopping processes depend on various control parameters. Numerical investigation of the lattice gas version of DDFT described here is now under way. A preliminary result was reported[38] and further results will be published[39].

5 Formally Exact Dynamical Density Functional Equation

In this section we describe a formally exact density functional equation for a classical system consisting of N particles of mass m with coordinates $\mathbf{r}^N \equiv \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N$ and momenta $\mathbf{p}^N \equiv \mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N$. Here we have adopted the convention of expressing N vectors associated with N particles by a single vector in $3N$ -dimensional space by attaching a superfix N . A point in the phase space $(\mathbf{r}^N, \mathbf{p}^N)$ is simply denoted by \hat{x} . The Liouville equation for the phase space dis-

⁴We should not forget that in the mapped kinetic Ising model, the lattice gas particle does not directly correspond to a real atom or a molecule, but the spin dynamics will reflect actual movements.

tribution function $\hat{D}(\hat{x}, t)$ is written as

$$\frac{\partial}{\partial t} \hat{D}(\hat{x}, t) = \hat{L}(\hat{x}) \hat{D}(\hat{x}, t) \quad (5.1)$$

Here and after we shall denote all the microscopic quantities by attaching $\hat{\cdot}$ to the symbol except for $\mathbf{r}_i, \mathbf{p}_i$ which carry particle labels. We shall often suppress arguments \hat{x} and simply write \hat{L} , etc instead of $\hat{L}(\hat{x})$, etc, and also abbreviate \hat{L}' , etc. for $\hat{L}(\hat{x}')$, etc. The technique used is now familiar projector method. Hence we introduce projector \hat{P} defined through its operation on an arbitrary phase space function $\hat{X}(\hat{x})$ as follows:

$$\hat{P} \hat{X}(\hat{x}) = \hat{\Pi}(\hat{x}) X\{\rho\} \quad (5.2)$$

where

$$X\{\rho\} \equiv \int d\hat{x} \delta\{\rho - \hat{\rho}\} \hat{X}(\hat{x}) \quad (5.3)$$

$$\hat{\Pi}(\hat{x}) \equiv \hat{D}_e(\hat{x}) / D_e\{\rho\} \quad (5.4)$$

and we have introduced the delta functional $\delta\{\rho_1 - \rho_2\}$ through the following functional integral expression valid for an arbitrary functional of the density $X\{\rho\}$:

$$\int d\{\rho_1\} \delta\{\rho_1 - \rho_2\} X\{\rho_1\} = X\{\rho_2\} \quad (5.5)$$

Here \hat{D}_e is the equilibrium phase space distribution function and D_e is the equilibrium density distribution functional. The relation between \hat{D}_e and D_e is the special case of the relation between the phase space distribution function $\hat{D}(\hat{x}, t)$ and the density distribution functional $D(\{\rho\}, t)$ as follows:

$$D(\{\rho\}, t) = \int d\hat{x} \delta\{\rho - \hat{\rho}(\hat{x})\} \hat{D}(\hat{x}, t) \quad (5.6)$$

This relation can be rewritten in terms of the projector:

$$\hat{\Pi}(\hat{x}) D(\{\rho\}, t) = \hat{P} \hat{D}(\hat{x}, t) \quad (5.7)$$

$\hat{\Pi}(\hat{x})$ is also expressed explicitly as

$$\hat{\Pi}(\hat{x}) = \Phi(\mathbf{p}^N) \exp[-\beta \hat{U}(\mathbf{r}^N) + \beta H\{\rho\}] \quad (5.8)$$

where $\Phi(\mathbf{p}^N)$ is the product of the normalized Maxwell momentum distribution functions of N particles, β^{-1} the Boltzmann constant times the absolute temperature, and $H\{\rho\}$ the free energy density functional introduced by the equation

corresponding to (6.13) below. $\Phi(\mathbf{p}^N)$ is normalized as

$$\int d\hat{x} \hat{\Pi}(\hat{x}) d\{\rho - \hat{\rho}\} = 1 \quad (5.9)$$

Since details of derivation of the exact DDFT equation is being given elsewhere, we only display the result. we have a formally exact equation of motion for the density probability distribution functional expressed in Laplace transform as

$$[z - \Gamma(\{\rho\}, z)] D^L(\{\rho\}, z) = D(\{\rho\}, 0) \quad (5.10)$$

where $D^L(\{\rho\}, z)$ is the Laplace transform of $D(\{\rho\}, t)$. Here the operator Γ defined through

$$\begin{aligned} \Gamma(\{\rho\}, z) X\{\rho\} &= \int d\{\rho'\} \int \int d\mathbf{r} d\mathbf{r}' \frac{\delta}{\delta \rho(\mathbf{r})} \\ &\int d\hat{x} \delta\{\rho - \hat{\rho}\} \left[\frac{\mathbf{p}^N}{m} \cdot \nabla^N \hat{\rho}(\mathbf{r}) \right] (z - \hat{Q} \hat{L})^{-1} \hat{Q} \hat{\Pi} \\ &\times \left[\frac{\mathbf{p}^N}{m} \cdot \nabla^N \hat{\rho}(\mathbf{r}') \right] \delta\{\hat{\rho} - \rho'\} \\ &\times \left[\frac{\delta}{\delta \rho'(\mathbf{r}')} + \frac{\delta \beta H\{\rho'\}}{\delta \rho'(\mathbf{r}')} \right] X\{\rho'\} \end{aligned} \quad (5.11)$$

We prefer to rewrite it as

$$\begin{aligned} \Gamma(\{\rho\}, z) X\{\rho\} &= \int d\{\rho'\} \int \int d\mathbf{r} d\mathbf{r}' \frac{\delta}{\delta \rho(\mathbf{r})} \\ &\times T_z(\mathbf{r}\mathbf{r}'; \{\rho\}\{\rho'\}) \left[\frac{\delta}{\delta \rho'(\mathbf{r}')} + \frac{\delta \beta H\{\rho'\}}{\delta \rho'(\mathbf{r}')} \right] \\ &\times X\{\rho'\} \end{aligned} \quad (5.12)$$

where

$$\begin{aligned} T_z(\mathbf{r}\mathbf{r}'; \{\rho\}\{\rho'\}) &\equiv \int d\mathbf{r}^N \delta\{\rho - \hat{\rho}\} [\nabla^N \hat{\rho}(\mathbf{r})] \\ &\cdot \Lambda_z(\mathbf{r}^N) \cdot [\nabla^N \hat{\rho}(\mathbf{r}')] \delta\{\hat{\rho} - \rho'\} \mathcal{D}_e(\mathbf{r}^N) \\ &\times D_e^{-1}(\{\rho'\}) \end{aligned} \quad (5.13)$$

and

$$\Lambda_z(\mathbf{r}^N) \equiv \int d\mathbf{p}^N \frac{\mathbf{p}^N}{m} (z - \hat{Q} \hat{L})^{-1} \hat{Q} \frac{\mathbf{p}^N}{m} \hat{\Phi}(\mathbf{p}^N) \quad (5.14)$$

It is some times more convenient to use

$$\begin{aligned} \tilde{\Lambda}_z(\mathbf{r}^N) &\equiv \mathcal{D}_e(\mathbf{r}^N) \Lambda_z(\mathbf{r}^N) \mathcal{D}_e(\mathbf{r}^N)^{-1} \\ &= \int d\mathbf{p}^N \hat{\Phi}(\mathbf{p}^N) \frac{\mathbf{p}^N}{m} (z - \hat{Q} \hat{L})^{-1} \hat{Q} \\ &\times \frac{\mathbf{p}^N}{m} \end{aligned} \quad (5.15)$$

where $\tilde{Q} \equiv 1 - \tilde{P}$ with \tilde{P} defined through

$$\tilde{P} \equiv \hat{D}_e^{-1} \hat{P} \hat{D}_e$$

or

$$\tilde{P} \hat{X}(\hat{x}) = D_e\{\hat{\rho}\}^{-1} \int d\hat{x}' \delta\{\rho - \hat{\rho}'\} \hat{D}_e(\hat{x}') \hat{X}(\hat{x}') \quad (5.16)$$

and $\mathcal{D}_e(\mathbf{r}^N)$ is the normalized equilibrium distribution function of the particle configuration \mathbf{r}^N . $\Lambda_z(\mathbf{r}^N)$ or $\tilde{\Lambda}_z(\mathbf{r}^N)$ can be interpreted as operators describing diffusion process occurring in the $3N$ -dimensional space \mathbf{r}^N .

Since the equation (5.10), though exact, is rather complicated, we simplify it by introducing some drastic approximations. The first one is based on the consideration that if we want to focus on the long time dynamics of density fluctuations, the momentum variables entering $\Gamma(\{\rho\}, z)$, (5.11), relaxes rapidly in a short time during which the density variable remains unchanged. In that case, we may simply replace the operator $(z - \hat{Q}\hat{L})^{-1}\hat{Q}$ by τ , the momentum relaxation time. This amounts to replacing $\Lambda_z(\mathbf{r}^N)$ or $\tilde{\Lambda}_z(\mathbf{r}^N)$ by $k_B T \tau \mathbf{1}_{3N}$ where $\mathbf{1}_{3N}$ is the unit tensor in the $3N$ -dimensional space \mathbf{r}^N . The momenta can be readily integrated out to give

$$\begin{aligned} \Gamma(\{\rho\}, z) \rightarrow & \frac{\tau}{m\beta} \int \int d\mathbf{r} d\mathbf{r}' \frac{\delta}{\delta\rho(\mathbf{r})} \\ & \times \int d\mathbf{r}^N \delta\{\rho - \hat{\rho}\} \sum_{i=1}^N [\nabla_i \hat{\rho}(\mathbf{r})] \cdot \\ & \times [\nabla_i \hat{\rho}(\mathbf{r}')] \\ & \times \exp[-\beta H\{\hat{\rho}\} + \beta H\{\rho\}] \\ & \times \left[\frac{\delta}{\delta\rho(\mathbf{r}')} + \frac{\delta\beta H\{\rho\}}{\delta\rho(\mathbf{r}')} \right] \quad (5.17) \end{aligned}$$

The last two steps above may be regarded as a kind of coarse-graining over short time scales.

So far we have not specified the functional form of $\hat{\rho}(\mathbf{r})$. The above expression becomes simpler if we take

$$\hat{\rho}(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \quad (5.18)$$

and we obtain for $\Gamma(\{\rho\}, z)$ which can now be denoted as $\Gamma\{\rho\}$ since there is no z dependence,

$$\begin{aligned} \Gamma\{\rho\} = & -\frac{\tau}{m\beta} \int d\mathbf{r} \frac{\delta}{\delta\rho(\mathbf{r})} \nabla \cdot \rho(\mathbf{r}) \nabla \\ & \times \left[\frac{\delta}{\delta\rho(\mathbf{r})} + \frac{\delta\beta H\{\rho\}}{\delta\rho(\mathbf{r})} \right] \quad (5.19) \end{aligned}$$

The equation (5.10) now takes the following form after transforming back to the time variable,

$$\frac{\partial}{\partial t} D(\{\rho\}, t) = \Gamma\{\rho\} D(\{\rho\}, t) \quad (5.20)$$

This is precisely the dynamical density functional equation mentioned in the preceding section.

Here we have not discussed about coarse-graining of the density function. Thus without coarse-graining the density profile has the same information as the N particle configuration since labelling of particles are irrelevant. One suggestion of coarse-graining comes from the normal mode analyses of liquids recently put forward by T. Keyes and others[40]. It seems natural that the variables describing stable directions associated with real frequencies can be projected out.

6 Derivation of DDFT equation for kinetic Ising model

We consider derivation of DDFT equation for kinetic Ising models. The system consists of N spins $\sigma_i = \pm 1$ on the N lattice sites labelled $i = 1, 2, \dots, N$. The entirety of N spin is simply denoted as $\hat{\sigma}$ which also denotes a microscopic state of the entire system. Change of a microscopic state consists of flipping of a cluster α of spins denoted as $\{\sigma\}_\alpha \rightarrow \{-\sigma\}_\alpha$. Here a cluster is an arbitrary set of spins which need not be connected by nearest neighbor bonds. The transition probability of this spin flip is denoted as $w_\alpha(\hat{\sigma})$. It is also convenient to introduce the cluster spin flip operator \hat{S}_α which acts on any function of spins $\hat{X}(\hat{\sigma})$ by

$$\hat{S}_\alpha \hat{X}(\hat{\sigma}) = \hat{X}(\{-\sigma\}_\alpha, \cdot) \quad (6.1)$$

where a center dot indicates a set of spins not involved in the transition. Here and after we often use hatted symbols to denote functions of microscopic spin state $\hat{\sigma}$. Our general kinetic Ising model is then expressed by the following master equation for the microscopic probability distribution function of the system spin configuration (the state distribution function) $\hat{D}_t(\hat{\sigma})$ as

$$\frac{\partial}{\partial t} \hat{D}_t(\hat{\sigma}) = \hat{L}_I(\hat{\sigma}) \hat{D}_t(\hat{\sigma}) \quad (6.2)$$

where

$$\hat{L}_I(\hat{\sigma}) \equiv \sum_{\alpha} (\hat{S}_\alpha - 1) \hat{w}_\alpha(\hat{\sigma}) \quad (6.3)$$

The detailed balance condition (DBC) is expressed as

$$\hat{S}_\alpha \hat{w}_\alpha(\hat{\sigma}) \hat{D}_e(\hat{\sigma}) \cdots = \hat{w}_\alpha(\hat{\sigma}) \hat{D}_e(\hat{\sigma}) \hat{S}_\alpha \cdots \quad (6.4)$$

Since the adjoint operator \hat{L}_I^\dagger of \hat{L}_I is given by $\hat{L}_I^\dagger = \sum_\alpha \hat{w}_\alpha(\hat{\sigma})(\hat{S}_\alpha - 1)$ we immediately find

$$\hat{D}_e \hat{L}_I^\dagger \hat{D}_e^{-1} = \hat{L}_I \quad (6.5)$$

where \hat{D}_e is the equilibrium state distribution function of the form,

$$\hat{D}_e(\hat{\sigma}) \equiv \exp[-\beta \hat{U}(\hat{\sigma})] \quad (6.6)$$

$\hat{U}(\hat{\sigma})$ being the state energy. Here and after we often suppress the argument $\hat{\sigma}$. In order to introduce the density variable we divide the lattice system into coarse-graining cells of the volume v labelled by a, b, \dots . The cell size should be such that a single cell contains a large number of lattice sites so that the density variable $\hat{\rho}_a$ defined below is quasi continuous. Here we define

$$\hat{\rho}_a \equiv \frac{1}{v} \sum_i^a \frac{1 + \sigma_i}{2} \quad (6.7)$$

where the sum runs over all the lattice sites contained in the cell a . With this we introduce the density probability distribution by

$$D_t[\rho] \equiv \sum_{\hat{\sigma}} \Delta[\rho - \hat{\rho}(\hat{\sigma})] \hat{D}_t(\hat{\sigma}) \quad (6.8)$$

where $[\rho]$ is the set of density variables ρ_a for all the cells a and

$$\Delta[\rho] \equiv \prod_a \Delta(\rho_a) \quad (6.9)$$

$\Delta(\rho_a)$ being Kronecker's delta equal to 1 or 0 according to $\rho_a = 0$ or otherwise, respectively. Here we introduce a projector \hat{P} by its operation on any state function $\hat{X}(\hat{\sigma})$ as

$$\hat{P} \hat{X}(\hat{\sigma}) = \hat{\Pi}(\hat{\sigma}) X[\hat{\rho}] \quad (6.10)$$

where

$$X[\hat{\rho}] \equiv \sum_{\hat{\sigma}} \Delta[\hat{\rho} - \hat{\rho}(\hat{\sigma})] \hat{X}(\hat{\sigma}) \quad (6.11)$$

and

$$\hat{\Pi}(\hat{\sigma}) \equiv \hat{D}_e(\hat{\sigma}) / D_e[\hat{\rho}] \quad (6.12)$$

Here $D_e[\rho]$ is the equilibrium density distribution related to \hat{D}_e exactly like (6.11) and we can

introduce the free energy density functional $H[\rho]$ by

$$H[\rho] \equiv -\beta^{-1} \ln D_e[\rho] \quad (6.13)$$

Here we list useful formulae involving the projector:

$$\begin{aligned} \sum_{\hat{\sigma}} \hat{P} \hat{X}(\hat{\sigma}) &= \sum_{\hat{\sigma}} \hat{X}(\hat{\sigma}), \hat{P} \hat{D}_e(\hat{\sigma}) X[\hat{\rho}] \\ &= \hat{D}_e(\hat{\sigma}) X[\hat{\rho}] \end{aligned} \quad (6.14)$$

We found it convenient to work with the Laplace transform of any function X_t of t defined by

$$X_z^L \equiv \int_0^\infty dt e^{-zt} X_t \quad (6.15)$$

Thus we have, for instance,

$$\hat{D}_z^L(\hat{\sigma}) = (z - \hat{L}_I)^{-1} \hat{D}_0(\hat{\sigma}) \quad (6.16)$$

As usual with projector technique we choose the initial state distribution function to satisfy $\hat{D}_0(\hat{\sigma}) = \hat{P} \hat{D}_0(\hat{\sigma})$. That is, we take

$$\hat{D}_0(\hat{\sigma}) = \hat{\Pi}(\hat{\sigma}) D_0[\hat{\rho}] \quad (6.17)$$

$D_0[\rho]$ being the initial density probability distribution. We then find

$$\begin{aligned} D_z^L[\rho] &= \sum_{\hat{\sigma}} \Delta[\rho - \hat{\rho}(\hat{\sigma})] (z - \hat{L}_I)^{-1} \hat{\Pi} D_0[\hat{\rho}] \\ &= \sum_{\hat{\sigma}} \Delta[\rho - \hat{\rho}(\hat{\sigma})] \hat{P} (z - \hat{L}_I)^{-1} \\ &\quad \times \hat{P} \hat{\Pi} D_0[\hat{\rho}] \end{aligned} \quad (6.18)$$

where the properties (6.14) have been used to obtain the second member. We can now use the following operator identity which we have used frequently with $\hat{Q} \equiv 1 - \hat{P}$:

$$\begin{aligned} \hat{P} (z - \hat{L}_I)^{-1} \hat{P} &= \{z - \hat{P} \hat{L}_I \hat{P} - \hat{P} \hat{L}_I (z - \hat{Q} \hat{L}_I)^{-1} \\ &\quad \times \hat{Q} \hat{L}_I \hat{P}\}^{-1} \hat{P} \end{aligned} \quad (6.19)$$

in (6.18), and retain only the contribution coming from $\hat{P} \hat{L}_I \hat{P}$ in the denominator on the rhs of (6.19). Then

$$D_z^L[\rho] \approx \sum_{\hat{\sigma}} \Delta[\rho - \hat{\rho}(\hat{\sigma})] (z - \hat{P} \hat{L}_I \hat{P})^{-1} \hat{P} \hat{\Pi} D_0[\hat{\rho}] \quad (6.20)$$

This amounts to the local equilibrium approximation introduced long ago[55]. The validity of this approximation was examined very recently for a spin glass model and found to be

reasonable[56]. Let us now consider

$$\begin{aligned}
 \hat{P}\hat{L}_I\hat{P}\hat{X} &= \hat{P}\hat{L}_I\hat{\Pi}\hat{D}_eX[\hat{\rho}] \\
 &= \hat{\Pi}\sum_{\hat{\sigma}'}\Delta[\hat{\rho}-\hat{\rho}']\hat{L}_I'\hat{D}_e'X[\hat{\rho}'] \\
 &= \hat{D}_e\sum_{\hat{\sigma}'}\Delta[\hat{\rho}-\hat{\rho}']D_e[\hat{\rho}']^{-1}\hat{L}_I'\hat{D}_e'X[\hat{\rho}'] \\
 &= \hat{D}_e\Gamma^\dagger[\hat{\rho}]X[\hat{\rho}] \\
 &= \hat{D}_e\sum_{[\rho]}\Gamma^\dagger[\rho|\hat{\rho}]X[\rho] \quad (6.21)
 \end{aligned}$$

where we have introduced the adjoint operator $\Gamma^\dagger[\rho]$. The $[\rho]-[\rho']$ element of its matrix representation is given by

$$\begin{aligned}
 \Gamma^\dagger[\rho|\rho'] &\equiv \sum_{\hat{\sigma}}\Delta[\rho-\hat{\rho}]\hat{D}_e[\hat{\rho}]^{-1}\hat{L}_I\hat{D}_e\Delta[\rho'-\hat{\rho}] \\
 &= \Gamma[\rho'|\rho] \quad (6.22)
 \end{aligned}$$

Repeatedly using (6.21) we find for an arbitrary algebraic function $F(x)$,

$$F(\hat{P}\hat{L}_I\hat{P})\hat{X} = \hat{D}_eF(\Gamma^\dagger[\hat{\rho}])X[\hat{\rho}] \quad (6.23)$$

$D_t[\rho]$ is then shown to satisfy the following equation:

$$\frac{\partial}{\partial t}D_t[\rho] = \Gamma[\rho]D_t[\rho] \quad (6.24)$$

We now transform $\Gamma[\rho|\rho']$ into a more transparent form by first rewriting it as

$$\Gamma[\rho|\rho'] = \sum_{\hat{\sigma}}\Delta[\rho'-\hat{\rho}]D_e[\rho']^{-1}\hat{L}_I\hat{D}_e\Delta[\rho-\hat{\rho}] \quad (6.25)$$

Remembering the definition $\hat{L}_I(\hat{\sigma}) \equiv \sum_{\alpha}(\hat{S}_{\alpha}-1)\hat{w}_{\alpha}(\hat{\sigma})$, (6.3), and DBC, (6.4), we obtain useful formulae for arbitrary \hat{X} and \hat{Y} :

$$\begin{aligned}
 &\sum_{\hat{\sigma}}\hat{\sigma}\hat{X}\hat{L}_I\hat{D}_e\hat{Y} \\
 &= \sum_{\alpha}\sum_{\hat{\sigma}}\hat{\sigma}\hat{X}(\hat{S}_{\alpha}-1)\hat{w}_{\alpha}\hat{D}_e\hat{Y} \\
 &= \sum_{\alpha}\sum_{\hat{\sigma}}\hat{X}\hat{w}_{\alpha}\hat{D}_e(\hat{S}_{\alpha}-1)\hat{Y} \\
 &= \sum_{\alpha}\sum_{\hat{\sigma}}\hat{S}_{\alpha}\hat{X}\hat{w}_{\alpha}\hat{D}_e(\hat{S}_{\alpha}-1)\hat{Y} \\
 &= \sum_{\alpha}\sum_{\hat{\sigma}}(\hat{S}_{\alpha}\hat{X})\hat{w}_{\alpha}\hat{D}_e\hat{S}_{\alpha}(\hat{S}_{\alpha}-1)\hat{Y} \\
 &= \sum_{\alpha}\sum_{\hat{\sigma}}(\hat{S}_{\alpha}\hat{X})\hat{w}_{\alpha}\hat{D}_e(1-\hat{S}_{\alpha})\hat{Y} \\
 &= -\frac{1}{2}\sum_{\alpha}\sum_{\hat{\sigma}}[(1-\hat{S}_{\alpha})\hat{X}] \\
 &\quad \times [(1-\hat{S}_{\alpha})\hat{Y}]\hat{w}_{\alpha}\hat{D}_e \quad (6.26)
 \end{aligned}$$

Using the above formulae we can write

$$\begin{aligned}
 \Gamma[\rho|\rho'] &= -\frac{1}{2}\sum_{\alpha}\sum_{\hat{\sigma}}[(1-\hat{S}_{\alpha})\Delta[\rho'-\hat{\rho}]] \\
 &\quad \times [(1-\hat{S}_{\alpha})\Delta[\rho\hat{\rho}]]\hat{w}_{\alpha}\hat{D}_e \quad (6.27)
 \end{aligned}$$

We notice that DBC for Γ is expressed in the following operator form:

$$\Gamma D_e = D_e \Gamma^\dagger \quad (6.28)$$

Now, changes in the density due to spin flip are

$$\begin{aligned}
 \delta^{\alpha}\hat{\rho}_{\alpha} &\equiv (\hat{S}_{\alpha}-1)\hat{\rho}_{\alpha} \\
 \delta^{\alpha}\hat{\rho} &\equiv (\hat{S}_{\alpha}-1)\hat{\rho} \quad (6.29)
 \end{aligned}$$

which can be quite small if the coarse-graining volume v is chosen to be sufficiently large and a cluster of flipping spins is small. Therefore, we have

$$\begin{aligned}
 &(1-\hat{S}_{\alpha})\Delta[\rho-\hat{\rho}] \\
 &= \Delta[\rho-\hat{\rho}]\Delta[\rho-\hat{\rho}-\delta^{\alpha}\hat{\rho}] \\
 &= \sum_{\alpha}\delta^{\alpha}\hat{\rho}_{\alpha}\frac{\partial}{\partial\rho_{\alpha}}\Delta[\rho-\hat{\rho}] \\
 &\quad + (\text{higher order terms in } v^{-1}) \quad (6.30)
 \end{aligned}$$

With these results we obtain neglecting higher order terms in v^{-1} in (6.30),

$$\begin{aligned}
 \Gamma[\rho|\rho'] &= -\frac{1}{2}D_e[\rho']^{-1}\sum_{\alpha}\sum_b\frac{\partial}{\partial\rho_{\alpha}}\frac{\partial}{\partial\rho_b'}\Upsilon_{ab}[\rho] \\
 &\quad \times TD_e[\rho']\Delta[\rho-\rho'] \quad (6.31)
 \end{aligned}$$

where

$$\Upsilon_{ab}[\rho] \equiv \langle \sum_{\alpha}\delta^{\alpha}\hat{\rho}_{\alpha}\delta^{\alpha}\hat{\rho}_b\Delta[\rho-\hat{\rho}]\hat{w}_{\alpha} \rangle / TD_e[\rho] \quad (6.32)$$

Here we have denoted the equilibrium average over microscopic states by $\langle \rangle$. This is further transformed by using (6.13) as

$$\begin{aligned}
 \Gamma[\rho|\rho'] &= -\frac{1}{2}\sum_{\alpha}\sum_b\frac{\partial}{\partial\rho_{\alpha}}\Upsilon_{ab}[\rho] \\
 &\quad \times \left(T\frac{\partial}{\partial\rho_b'}\frac{\partial H[\rho']}{\partial\rho_b'} \right) \Delta[\rho-\rho'] \quad (6.33)
 \end{aligned}$$

The operators $\Gamma[\rho]$ or its adjoint $\Gamma^\dagger[\rho]$ is obtained through

$$\Gamma[\rho|\rho'] = \Gamma[\rho]\Delta[\rho-\rho'] = \Gamma^\dagger[\rho']\Delta[\rho-\rho'] \quad (6.34)$$

Therefore we find, for instance,

$$\Gamma[\rho] = \frac{1}{2} \sum_{ab} \frac{\partial}{\partial \rho_a} \Upsilon_{ab}[\rho] \left(T \frac{\partial}{\partial \rho_b} + \frac{\partial H[\rho]}{\partial \rho_b} \right) \quad (6.35)$$

This is to be used on the rhs of (6.24) to obtain the equation for $D_t[\rho]$.

From now on we specialize to the case where the total spin is conserved, that is, $\sum_a \delta^\alpha \hat{\rho}_a = 0$ for every cluster α . This implies $\sum_a \Upsilon_{ab}[\rho] = 0$. As a consequence we have

$$\Upsilon_{aa} = - \sum_{b \neq a} \Upsilon_{ab} \quad (6.36)$$

By splitting the sum over a, b in (6.35) into those with $a = b$ and those with $a \neq b$ and use (6.36) to those with $a = b$, we find

$$\Gamma[\rho] = \frac{1}{2} \sum_a \sum_{b \neq a} \frac{\partial}{\partial \rho_a} \Upsilon_{ab}[\rho] \left[T \left(\frac{\partial}{\partial \rho_b} - \frac{\partial}{\partial \rho_a} \right) + \frac{\partial H[\rho]}{\partial \rho_b} - \frac{\partial H[\rho]}{\partial \rho_a} \right]$$

Since the expression in $[\]$ on the rhs of the above expression changes sign under permutation of a and b whereas $\Upsilon_{ab}[\rho]$ is invariant, we can symmetrize this expression to obtain

$$\Gamma[\rho] = -\frac{1}{4} \sum_a \sum_{b \neq a} \left(\frac{\partial}{\partial \rho_a} - \frac{\partial}{\partial \rho_b} \right) \Upsilon_{ab}[\rho] \times \left[T \left(\frac{\partial}{\partial \rho_a} - \frac{\partial}{\partial \rho_b} \right) + \frac{\partial H[\rho]}{\partial \rho_a} - \frac{\partial H[\rho]}{\partial \rho_b} \right] \quad (6.37)$$

Now, if we choose a coarse-grained cell to contain enough number of lattice points so that the ρ 's are quasi-continuous, we obtain continuum versions of our equations. This can be done by the following transcriptions:

$$\frac{\partial}{\partial \rho_a} \rightarrow v \frac{\delta}{\delta \rho(\mathbf{r})}, \quad \sum_a \cdots \rightarrow \frac{1}{v} \int d\mathbf{r} \cdots, \quad v^2 \Upsilon_{ab}[\rho] \rightarrow \Upsilon_{\mathbf{r}, \mathbf{r}'}[\rho] \quad (6.38)$$

where \mathbf{r} and \mathbf{r}' indicate spatial locations of the cells a and b , respectively. The fact that in (6.37) the cells a, b are different is reflected by the fact that $\Upsilon_{\mathbf{r}, \mathbf{r}'}[\rho]$ is a smooth function as $\mathbf{r} \rightarrow \mathbf{r}'$. The continuum version of (6.37) is then

$$\Gamma[\rho] = -\frac{1}{4} \int d\mathbf{r} \int d\mathbf{r}' \left(\frac{\delta}{\delta \rho(\mathbf{r})} - \frac{\delta}{\delta \rho(\mathbf{r}')} \right) \times \Upsilon_{\mathbf{r}, \mathbf{r}'}[\rho] \left[T \left(\frac{\delta}{\delta \rho(\mathbf{r})} - \frac{\delta}{\delta \rho(\mathbf{r}')} \right) + \frac{\delta H[\rho]}{\delta \rho(\mathbf{r})} - \frac{\delta H[\rho]}{\delta \rho(\mathbf{r}')} \right] \quad (6.39)$$

This expression can be transformed into another form which directly corresponds to (6.35) if we allow singularity in Υ by defining

$$\tilde{\Upsilon}_{\mathbf{r}, \mathbf{r}'}[\rho] \equiv \Upsilon_{\mathbf{r}, \mathbf{r}'}[\rho] - \delta(\mathbf{r} - \mathbf{r}') \int d\mathbf{r}'' \Upsilon_{\mathbf{r}, \mathbf{r}''}[\rho] \quad (6.40)$$

and we find

$$\Gamma[\rho] = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{\delta}{\delta \rho(\mathbf{r})} \tilde{\Upsilon}_{\mathbf{r}, \mathbf{r}'}[\rho] \left[T \frac{\delta}{\delta \rho(\mathbf{r}')} + \frac{\delta H[\rho]}{\delta \rho(\mathbf{r}')} \right] \quad (6.41)$$

Continuum version of the conservation law is $\int d\mathbf{r} \tilde{\Upsilon}_{\mathbf{r}, \mathbf{r}'}[\rho] = 0$. Returning to (6.39), we simplify it by assuming that the range of $\Upsilon_{\mathbf{r}, \mathbf{r}'}[\rho]$ is small compared to the scale of spatial variation of the density. In this case (6.39) becomes

$$\Gamma[\rho] = -\frac{1}{4} \int d\mathbf{r} \int d\mathbf{r}' \left[(\mathbf{r}' - \mathbf{r}) \cdot \nabla \frac{\delta}{\delta \rho(\mathbf{r})} \right] \times \Upsilon_{\mathbf{r}, \mathbf{r}'}[\rho] (\mathbf{r}' - \mathbf{r}) \cdot \nabla \left[T \frac{\delta}{\delta \rho(\mathbf{r})} + \frac{\delta H[\rho]}{\delta \rho(\mathbf{r})} \right] \quad (6.42)$$

where ∇ inside $[\]$ to the left acts only inside of $[\]$. Assuming that $\Upsilon_{\mathbf{r}, \mathbf{r}'}[\rho]$ depends only on $|\mathbf{r} - \mathbf{r}'|$ which is consistent with our assumption of separation of the length scales just mentioned, (6.42) reduces to

$$\Gamma[\rho] = - \int d\mathbf{r} \frac{\delta}{\delta \rho(\mathbf{r})} \nabla \cdot \gamma_{\mathbf{r}}[\rho] \nabla \left[T \frac{\delta}{\delta \rho(\mathbf{r})} + \frac{\delta H[\rho]}{\delta \rho(\mathbf{r})} \right] \quad (6.43)$$

where, noting that $\Upsilon_{\mathbf{r}, \mathbf{r}'}[\rho]$ with $a \neq b$ is negative in general for spin exchange, we have defined

$$\gamma_{\mathbf{r}}[\rho] \equiv -\frac{1}{4} \int d\mathbf{r}' (x - x')^2 \Upsilon_{\mathbf{r}, \mathbf{r}'}[\rho] \quad (6.44)$$

For a spin pair exchange in which $\alpha = (i, j)$ with $i \in a, j \in b$ and $a \neq b$ to occur we can demand $\sigma_i \neq \sigma_j$, which can be taken care of by inserting a factor $\frac{1}{2}(1 - \sigma_i \sigma_j)$. Therefore, we can write for $a \neq b$,

$$\Upsilon_{ab}[\rho] = -\frac{1}{TD_e[\rho]} \left(\frac{1}{v^2} \sum_i^a \sum_j^b \hat{w}_{ij}(\hat{\sigma}) \frac{1 - \sigma_i \sigma_j}{2} \times \Delta[\rho - \hat{\rho}] \right) \quad (6.45)$$

If we use the lattice gas variable $n_i \equiv \frac{1}{2}(1 + \sigma_i) = 0$ or 1 , we have

$$\begin{aligned} \frac{1}{2}(1 - \sigma_i \sigma_j) &= n_i + n_j - 2n_i n_j \\ &= \frac{1}{2}[n_i(1 - n_j) + n_j(1 - n_i)] \end{aligned} \quad (6.46)$$

Therefore,

$$\begin{aligned} \Upsilon_{ab}[\rho] = & -\frac{1}{TD_e[\rho]} \left(\frac{1}{v^2} \sum_i^a \sum_j^b \hat{w}_{ij}(\hat{\sigma}) \right. \\ & \times \frac{n_i(1-n_j) + n_j(1-n_i)}{2} \Delta[\rho - \hat{\rho}] \Big) \end{aligned} \quad (6.47)$$

If we assume that $\frac{1}{2}[n_i(1-n_j) + n_j(1-n_i)]$ in the above expression can be replaced by a constant times $\rho(\rho_m - \rho)$, (ρ_m the lattice point density) in view of the presence of $\Delta[\rho - \hat{\rho}]$ and slow variation of $\rho(\mathbf{r})$ on the coarse graining length scale and also that $w_{ij}(\hat{\sigma})$ does not depend sensitively on $\hat{\rho}$, we will find that

$$\gamma_{\mathbf{r}}[\rho] \approx \text{const. } \rho(\mathbf{r})[\rho_m - \rho(\mathbf{r})] \quad (6.48)$$

In particular, since in our model we must choose $\rho(\mathbf{r})$ to be much smaller than ρ_m , we find

$$\gamma_{\mathbf{r}}[\rho] \approx \text{const. } \rho(\mathbf{r}) \quad (6.49)$$

Thus we have shown how we can map a spin exchange kinetic Ising model onto the DDFT equation (2.6). Finding relationships between kinetic Ising models and continuum dynamical models are useful in other respects as well. There are certain types of kinetic Ising models whose equilibrium properties are trivial, but kinetic constraints are incorporated in such a way that the models reproduce many features of glassy systems[57, 58, 59]. However, relationship of these models with reality is far from clear. Mapping of these models onto continuum models may enhance usefulness of these spin models in understanding real systems.

7 Epilogue

In this article the author presented some recent advances in our understanding of the problem of supercooled liquids and glass transitions, which is regarded as one of the remaining most challenging problems in condensed matter physics [53], from the heavily biased point of view by the author's own experience. The main emphasis is to describe an attempt to provide a wider framework incorporating the current MCT so as to approach the regime dominated by thermally activated processes. It is quite possible that in such a regime where only the extremely long time behavior is relevant, (equilibrium) statistical mechanics plus the detailed balance is everything[60]. However, it is still meaningful

to try to relate such a regime with a more fluid regime where MCT is relevant in a unified theoretical scheme.

It may well be that this field is going to be one of the areas of condensed matter physics where a continuum or field-theoretical treatment makes a great sense like phase transitions and soft condensed matter which are associated with such prominent names as Landau, Wilson, de Gennes and Edwards. At this time it is impossible to guess if there will be a final theory of structural glass transition, and if so, what form it will take. However, if there is going to be such a theory, I am confident that the kind of the first principle approach starting from MCT which I described here will be its indispensable ingredient.

I have come to realize that the problems of supercooled liquids and glass transitions offer new challenges to non-equilibrium statistical mechanics. We here mention some factors which can be internally related among each other:

- Existence of widely different time scales characterizing soft mode vibration and relaxation, β relaxation, α relaxation, thermally activated processes, and/or aging processes. Enormous change of time scale occurs at a very small change of static parameters such as density or temperature.
- Question of ergodicity and its break down, and possible violation of fluctuation-dissipation relations.
- Spontaneous appearance of frozen or long-lived short scale spatial heterogeneities.
- Question about absence or presence of an equilibrium phase transition underlying a glass transition.

Apart from supercooled liquids and glass transitions described here in some detail, the methodology that can be developed by coping with such difficult problems can become a useful tool to tackle other difficult problems of complex fluids such as dynamics of highly entangled polymer melt[61] or microemulsion systems[62].

The problems posed in this article should be also of interest to those mathematicians or mathematical physicists concerned with the foundation of statistical mechanics, for instance, those working on the large deviation theory [63]. Here is the problem in which usefulness of various nice mathematical frameworks can be put to severe tests because we really need concrete

answers to hard questions, not just more elegant or more rigorous rederivations of the results already known to physicists.

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[付記]

この記事を見てフォーマルな事が多く内容がないと感じられる向きもあると思うので、少しつけくわえる。これらの文章を書いた1997年は本文にも書いた様にそれまで欠けていたDDFTの微視的導出の必要性を感じていたのもそれに時間を掛けた。これを奇麗に一般的にやる道具としてプロジェクターしかないのも勢いフォーマルになってしまった。次はこれに肉付けして行く事であるが、いきなり普通の過冷却液体で微視的にやる事は計算機以外には手がない。一方MCTが成し遂げた重要な点は、ガラス転移にユニバーサルな性格があるとの認識を齎した事である。もともとMCTは単純液体の理論である。それが高分子に到るまでの複雑な系に適用されある程度成功している。又、低温の性質についても別のユニバーサリティがある事がわかっている。この様な事実の深い理由を探る事は重要である。そこでガラス的な振る舞いをする別の系に目を向ける事は有用であると思われる。思いつくままに例を挙げる。(1)物理ゲル：ゲル化が進んで動きが遅くなる過程がガラス転移との関連で議論されている。(Adam, Martin, Wilcoxon, Ren, Sorensen 等)。(2)ブロック共重合体：よく知られたミクロ相分離は必ずしも奇麗な相転移とはならず転移点近くでガラス的な乱れがある事が報告されている。(橋本ほか)。この問題は最近 Kivelson 等によって提唱されている過冷却液体やガラス転移にまつわるFLD (fluctuation-limited-domain) の考えを想起させる。考えてみればFLDはブロック共重合体や両親媒性の系で昔からあったアイデアある。(3)2元合金等の相分離における弾性効果：この問題は小貫等によって計算機で調べられ相分離にともなう弾性エネルギーの増加によって相分離過程が妨げられ、複雑なドメイン構造が出現する事がわかった。これらの問題の関連をみる一つの方法としてそれぞれの現象を支配する方程式を相互にマップする事が考えられる。この記事に書いたフォーマルな道具立てがこの様な事に役にたつ事があるかも知れない。

最後にガラスの分野にはいって3年余りになるが、最近感じている事を付け加える。構造ガラスの分野は歴史も古く応用上重要で物理といわず化学や工学など多彩なバックグラウンドの人がいて理論家はその一部に過ぎない。一方物理の理論で人気があるのはスピングラス(ポツグラスやp-spin系も含めた広い意味で)である。この分野は世界でもトップクラスの知性を集めている。丁度臨界現象でくりこみ群が出たころ素粒子論のトップの人たちが入り込んできところを彷彿させる。一方これに比較すると構造ガラスの理論家は、失礼になるかも知れないが、自分を含めて見劣りがするのは否めない。それがMCTの様なちゃんとした理論が多く注目を集める理由であろう。しかし実験的には構造ガラスの方がはるかに豊かで将来性があると思う。この分野の理論家として一つ方向はスピングラスで達成された深い理解を構造ガラスに移植する事であろう。この方向の研究はまだ少ない。しばらく前T. Kirkpatrick (SKモデルの人ではない!)等が精力的にやっていたが今は別の方に転じてしまった。極く最近Parisi一派が本気で取り組み始めた様に見えるのはencouragingである。しかし液体のダイナミクスは又別の側面があり単なる移植ではすまず、一筋縄では行かない事もあるに違いない。何れにしてもここに若い人たちがこれから取り組むべき大きな問題がある事を強調したい。